

FORM PTO-1390  
(REV 10-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

D078 1090

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/700099

INTERNATIONAL APPLICATION NO.

PCT/EP99/03229

INTERNATIONAL FILING DATE

11 May 1999

PRIORITY DATE CLAIMED

12 May 1998

TITLE OF INVENTION

LOW-EMISSION FLOOR COVERING

APPLICANT(S) FOR DO/EO/US

Fischer et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
  2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
  3. ☐ This is an express request to promptly begin national examination procedures (35 U.S.C. 371(f)).
  4. ☒ The US has been elected by the expiration of 19 months from the priority date (PCT Article 31).
  5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
    - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
    - b. ☐ has been communicated by the International Bureau.
    - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
  6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
    - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
    - b. ☐ have been communicated by the International Bureau.
    - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
    - d. ☒ have not been made and will not be made.
  8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
  9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). **Unsigned**
  10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11 to 16 below concern document(s) or information included:
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. ☒ A **FIRST** preliminary amendment.
  - ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
  14. ☐ A substitute specification.
  15. ☐ A change of power of attorney and/or address letter.
  16. ☒ Other items or information:
 

Form PCT/ISA/210  
Form PCT/IPEA/416  
Form PCT/IPEA/409  
Amended Claims and English translations thereof  
Copies of cited references

529 Rec'd PCT/PTC 09 NOV 2000

APPLICATION NO. (if known, see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO. PCT/EP99/03229		..... DOCKET NUMBER D078 1090	
17. The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00 <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>  	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ 0	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	24 - 20 =	4	X \$18.00	\$ 72.00	
Independent claims	1 - 3 =	0	X \$80.00	\$ 0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$ 0	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$ 932.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$ 0	
<b>SUBTOTAL =</b>				\$ 932.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ 0	
<b>TOTAL NATIONAL FEE =</b>				\$ 932.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$ 0	
<b>TOTAL FEES ENCLOSED =</b>				\$ 932.00	
				Amount to be	\$
				refunded:	
				charged:	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ 932.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 09-0528. A duplicate copy of this sheet is enclosed.					
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>					
SEND ALL CORRESPONDENCE TO: James F. Vaughan, Esq. Womble Carlyle Sandridge & Rice PLLC 1201 West Peachtree Street Suite 3500 Atlanta, GA 30309 Telephone (404) 872-7000 Fax (404) 888-7490					
				SIGNATURE:	
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				REGISTRATION NUMBER	

Form PTO-1390 (REV 10-2000) page 2 of 2 Express Mail: I hereby certify that this correspondence is being deposited with the United States Postal Service as "Express Mail Post Office to Addressee," in an envelope addressed to: Assistant Commissioner for Patents, Box PCT, Washington, D.C. 20231 on November 9, 2000. Express Mail No.: EL440468089

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Application of: )  
)  
    **Bernd Fischer and Stefan Kolbig** )      Examiner: Unknown  
)  
Serial No.:   **To Be Determined** )      Art Unit: Unknown  
              (National Phase of PCT/EP99/03229) )  
)  
Filed:       **Herewith** )  
)      Docket No.: **D078 1090**  
For:   **LOW-EMISSION FLOOR COVERING** )  
)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Box PCT  
Washington, D.C. 20231

Sir:

Please amend the subject application as follows:

IN THE CLAIMS

Please amend claims 3, 4, 6, 7, 10, 11, 13, 15-17 as follows:

3.       (Amended)   Floor covering as claimed in Claim [1 or 2] 1, wherein  
the polyolefin is selected from among the class of VLD PE polymers.

4.       (Amended)   Floor covering as claimed in [any one of Claims 1 to 3]

Claim 1, wherein the polyolefin is a mixture of at least two ethylene copolymers,  
wherein the ethylene copolymer mixture comprises a copolymer (a) as the main  
polymer with a density of 0.89 – 0.91 g/cm<sup>3</sup> and a copolymer (b) to control rheology  
and elasticity with a density of 0.86–0.88 g/cm<sup>3</sup> and an MFI > 3.

6. (Amended) Floor covering as claimed in [Claims 4 and 5] Claim 4, wherein the copolymers (a) and (b) are copolymers of ethylene and octene.

7. (Amended) Floor covering as claimed in [any one of Claims 1 to 6] Claim 1, wherein the grafted copolymer is a grafted copolymer based on a HD polyethylene.

10. (Amended) Floor covering as claimed in [any one of Claims 1 to 9] Claim 1, wherein the proportion of grafted copolymer in relation to the total weight of the polymeric binder is 5% to 25% by weight.

11. (Amended) Floor covering as claimed in [any one of Claims 1 to 10] Claim 1, wherein the elastomer is cross-linked with at least one cross-linking agent based on organic peroxides and possibly one or more co-cross-linking agents.

13. (Amended) Floor covering as claimed in [any one of Claims 1 to 12] Claim 1, which further contains fillers and/or pigments as well as possibly processing aids, antioxidants, static eliminators, UV stabilizers and slip agents.

15. (Amended) Floor covering as claimed in [any one of Claims 1 to 14] Claim 1, having a variable color pattern and a homogeneous design.

16. (Amended) Process for producing a floor covering as claimed in [any one of Claims 1 to 15] Claim 1, comprising the provision of a substrate in the form of a strip and the application of the elastomers defined in [Claims 1 to 14] Claim 1 to one side of the substrate.

17. (Amended) Process for producing a floor covering as claimed in [any one of Claims 1 to 15] Claim 1 comprising the following steps:

- (a) compounding of the polymeric material defined in [Claims 1 to 14] Claim 1 to produce a ground or granulate material;
- (b) wetting of particles with a solution containing at least one organic peroxide free from aromatic hydrocarbons and possibly one or several co-cross-linking agents and possibly process oil, wherein the particles contain the above-defined polymers, which form the polymeric binder of the floor covering according to the invention, either cross-linked or partially cross-linked in the form of a ground or granulate stock,
- (c) heating of the particles to a temperature at which the peroxide has sufficiently long stability, wherein the particles are subsequently precompacted and shaped into a flat product, and
- (d) pressing of the flat product thus obtained in a suitable apparatus at a temperature at which the half-life of the peroxide is reduced such that cross-linking initiated by the peroxide simultaneously occurs to obtain a flat end product.

Please add new claims 19-24 as follows:

19. Process as claimed in Claim 17, wherein the mass in step (a) is compounded, in addition, with a chemical expanding agent.

20. Process as claimed in Claim 19, wherein, after cross-linking under pressure in step (d), foaming of the material is effected by releasing the pressure at a further increased temperature.

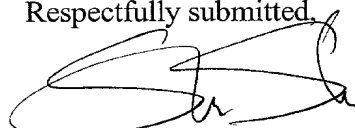
21. Process as claimed in Claim 19, wherein the chemical expanding agent is a sulfohydrazide or azodicarbonamide or a combination thereof.

22. Process as claimed in Claim 17, comprising the following steps:
- (a) compounding of the polymeric material defined in Claim 1 together with additives, fillers, peroxide, co-cross-linking agents and a chemical expanding agent;
  - (b) partial cross-linking and foaming of the mixture in an extruder;
  - (c) discharging of the foam through an extruder nozzle into a water bath and granulating of the slab thus formed; and
  - (d) further grinding and drying of the granulate, which is then wetted with a mixture of liquid peroxide, co-cross-linking agents and mineral oil, wherein the ground stock is subsequently distributed over a release paper and covered with an anti-adhesive paper and is fed into a heated press, with the temperature and pressure adjusted such that the particle bed along the heating surfaces becomes plastic and melts to form a closed surface and at the same time the temperature initiates the decomposition of the peroxide, whereby the outer layers simultaneously cross-link, so that a floor covering with integral structure is obtained.

23. Process as claimed in Claim 19, wherein the back of the covering is ground for sizing in a post-treatment step.

24. Process as claimed in Claim 17, wherein the structure of the cross-linked material is revealed after exposing the surface by grinding and/or splitting.

Respectfully submitted,



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Pauze Parson Britt  
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**Low-Emission Floor Covering****Description**

The present invention relates to a floor covering, which has excellent wear resistance and essentially causes no malodorous and/or health impairing emissions and is not subject to color changes due to aging over a longer period of time, as well as a process for manufacturing the same.

Rubber-based elastomer floor coverings are among the high-performance floor coverings due to their durability and wide range of applications. However, vulcanization and process additives or agents tend to be released from the floor covering in unchanged or chemically changed form.

Typically, vulcanizable rubbers of a wide variety of types are used as polymeric binders for floor coverings. These rubbers include primarily SBR, NR, IR, IIR and NBR, the cross-linkage of which is achieved by cross-linking agents, such as sulfur, in conjunction with vulcanization additives. Such vulcanization additives include vulcanization accelerators, e.g., mercapto compounds, sulfenamides, thiuram, guanidine, dithiocarbamates and amines, vulcanization retarders, e.g., phthalic acid anhydride and N-cyclohexylthiophthalimide, antioxidants, e.g., 2-mercaptobenzimidazole, masticating agents, e.g., 2,2'-dibenzamidodiphenyl-disulfide, softeners or process oils, reinforcing resins, e.g., phenol formaldehyde resin, and in part vulcanization activators, e.g., zinc oxide. These vulcanizing agents and additives are not completely converted in the vulcanization process. As a result, these additives or their byproducts produced in the vulcanization process partly remain in the system or are released from this rubber system. This emission process may continue over a relatively long time. In floor coverings, this occurs especially when they are taken out of their packaging and by means of



adhesives are fixed to the floor on a suitable substrate. Temperature, air humidity and ventilation of the room further influence the progress of the emission process.

Generally, the vulcanization additives or their byproducts produced during the vulcanization process, which are released from the rubber system, cause an unpleasant odor and are a health hazard at certain concentrations. It has also been shown that substances released from rubber floor coverings may cause white walls (plaster, wall paint, etc.) to yellow. Furthermore, these rubber-based elastomer floor coverings are subject to aging, which negatively affects the color of a patterned floor covering, e.g., by yellowing.

Thus, the object of the present invention is to provide a wear-resistant, low-emission, non-aging and variably color-patterned floor covering with an attractive appearance having elastomeric, rubber-like properties without the presence of rubber vulcanized with sulfur or sulfur compounds.

This object is attained by the embodiments characterized in the claims. In particular, a floor covering is provided comprising at least one elastomer as polymeric binder based on at least one polyolefin with a density  $< 0.910 \text{ g/cm}^3$  and at least one graft copolymer. Preferably, a polyolefin with a density ranging from  $0.85 - 0.91 \text{ g/cm}^3$ , particularly preferably from  $0.85 - 0.892 \text{ g/cm}^3$  is used. The polyolefin is preferably selected from among the class of the VLD PE polymers.

According to a preferred embodiment, the polyolefin is a mixture of at least two ethylene copolymers, wherein the ethylene copolymer comprises a copolymer (a) as the main polymer with a density of  $0.89 - 0.91 \text{ g/cm}^3$  and, a copolymer (b) to control rheology and elasticity with a density of  $0.86 - 0.88 \text{ g/cm}^3$  and a MFI  $> 3$  (at  $190^\circ\text{C}$ ; 2.16 kg).

For example, the copolymers (a) and (b) are copolymers of ethylene and octene. The copolymers (a) and (b) can be present, for example at a weight ratio of 4:1 to 3:2.

To increase wear resistance, the polymeric binder contains as a further component at least one graft copolymer, preferably based on a HD polyethylene. In particular, the graft copolymer can be a HD polyethylene grafted with maleic acid anhydride, where the grafting degree is preferably 1% to 5%. The proportion of graft copolymer is, for example, 5% to 25% by weight in relation to the total weight of the polymeric binder. Accordingly, the proportion of the at least one polyolefin, which in addition to the graft copolymer constitutes the polymeric binder of the floor covering according to the invention, is between 75% to 95% by weight in relation to the total weight of polymeric binder.

The polymers used to construct the floor covering according to the invention, i.e., the at least one polyolefin in combination with the at least one graft copolymer is cross-linked with at least one suitable cross-linking agent based on organic peroxides, particularly organic peroxides free from aromatic hydrocarbons, and possibly one or several co-cross-linking agents. An example of a suitable organic peroxide, free from aromatic hydrocarbons, is the commercially available DHBP (2,5-dimethyl-2,5-di(tert.butylperoxy)hexane). Isocyanuric acid derivatives and/or acrylate or methacrylate derivatives, derived from polyols, may be used as co-cross-linking agents. Particularly preferred as a cross-linking agent, this is a mixture of one part by weight of organic peroxide free from aromatic hydrocarbons, two parts by weight of trimethylolpropane trimethacrylate (TRIM) and one part per weight of triallyl isocyanurate (TAIC). TRIM influences the hardness and the indentation characteristics of the elastomer constituting the floor covering according to the invention, whereas TAIC has a positive effect on the cross-linking rate.

Polyolefins suitable for use in the floor covering according to the invention are, for example, the following commercially available polymers: DOW DSH 1500, DOW DSH 8501, Exxon Exact 4041 and Exxon Exact 4033. Preferred components for the aforementioned ethylene copolymer are, for example, DOW DSH 1505 as copolymer (a) and DOW EG 8200 as additional copolymer (b), which may be used to control rheology and elasticity. A suitable graft copolymer for use in the floor covering according to the invention is, for example, the commercially available polymer DOW XU 60769.07.

The floor covering according to the invention can furthermore contain fillers or a mixture thereof, particularly a mixture of platelet-shaped and crystalline mineral intergrowths, which as reinforcing fillers substantially contribute to the properties, particularly to the mechanical properties, of the floor covering according to the invention. The filler amount used is 35% to 60% by weight in relation to the total weight of the composition or formulation forming the floor covering according to the invention, where a minimum proportion of platelet-shaped filler particles is necessary to reach higher filler amounts. Examples of such fillers are:

- Sillitin, available from Hofmann Mineral,
- Doltitan 2, available from PETROCHEM K. Zafranias S.A.,
- Inducarb 2, available from Omya, or
- Kronos 2200, available from Kronos Titan.

Other fillers, which the floor covering according to the invention may contain, are for example:

Filler	Type (e.g.)	Supplier
Quartz powder	Sirkon SF 300	Quarzwerte GmbH
Kaolin	Nucap EDL 200	Lehmann & Voss & Co.
Talcum	Alpha Talc CT 6/46	Alpha-Calcit Füllstoffe GmbH KG

Wood flour	Holzmühle Westerkamp & Co.	Wood flour Type 120
Dolomite	KL 30	Naintsch Mineralwerke Graz
Aluminum trihydroxide	Martinal ON 313	Martinswerk GmbH
Precipitated silicic acid	P 820	Degussa AG
Heavy spar	Heavy spar TS	Sachtleben GmbH
Chalk	Omyacarb 6	Omya

Furthermore, depending on the color adjustment, the floor covering according to the invention may contain the following inorganic pigments:

Pigments	Supplier
Kronos 2200	Kronos Titan
Bayferrox 140	Bayer AG
Bayferrox 830	Bayer AG
Hostaprint A2 R 31	Clariant

Where indicated, the floor covering according to the invention may also contain conventional processing agents. The following are examples of such processing agents:

Slip Additives	Type (e.g.)	Supplier
Ca stearate	Ceasit 1	Bärlocher GmbH
Ester wax	OP wax	Clariant

In addition, antioxidants, UV stabilizers and the like may be contained:

Stabilizers	Type (e.g.,)	Supplier
Antioxidants	Irganox 1010	Ciba Geigy AG
UV stabilizers	Chimassorb 944 FI	Ciba Geigy AG

Based on the elastomer used as polymeric binder according to the invention, the inventive floor covering exhibits practically no malodorous and/or health impairing emissions, in contrast to the known floor coverings that use rubbers (SBR) as elastomers. In addition, the floor covering according to the invention has excellent abrasion resistance compared to the known rubber-based floor coverings. Due to the subsequent cross-linkage of the polymers constituting the, at least, one elastomer and used as polymeric binder in the floor covering according to the invention, it is possible, surprisingly, to increase the filler amount in the floor covering up to 60% by weight in relation to the total weight of the composition or formulation forming the floor covering according to the invention while maintaining excellent wear behavior.

Surprisingly, the surface energy of the floor covering thus produced can be very readily increased by a corona treatment, so that a primer exhibits very good adhesion resulting in better bondability compared to rubber floor coverings. Surprisingly, it was also found that the floor covering according to the invention is less subject to color changes (yellowing) during its life. Thus, it is possible to achieve sufficiently flexible pattern and color design possibilities, adequate resistance to aging and low emission loads while nevertheless retaining the desired elastomeric properties.

A further subject of the present invention is a process for producing the floor covering according to the invention comprising the provision of substrates in the form of strips and the application of the above-defined elastomer to one side of the substrate.

For the substrate, any material currently used in floor coverings and based on natural and/or synthetic woven or knit fabrics, textile materials as well as fleece or nonwovens may be used. For example, jute fabrics or blends of natural fibers, such as cotton and staple fibers, glass fiber fabrics, glass fiber fabrics coated with adhesion promoters, synthetic blends, fabrics made of core/sheath fibers, e.g., with a polyester core and a polyamide sheath.

Furthermore, a novel process for manufacturing a low-emission, particularly homogenous floor covering is provided, comprising essentially the following steps:

- Wetting of particles with a solution containing at least one organic peroxide free from aromatic hydrocarbons and possibly one or more co-cross-linking agents and possibly process oil, where the particles contain the above-defined polymers forming the polymeric binder of the floor covering according to the invention, either uncross-linked or partially cross-linked, in the form of a ground or granulate stock,
- Heating of the particles to a temperature at which the peroxide has sufficiently long stability, and subsequent compaction of the particles and shaping into a flat product, and
- Pressing of the flat product thus obtained in a suitable apparatus at a temperature at which the half-life of the peroxide is reduced, such that cross-linking initiated by the peroxide simultaneously occurs, to obtain a flat final product.

In particular, the process according to the invention, in a preferred embodiment, can comprise the following steps (a) to (d). In step (a) a cross-linkable mass containing the above-defined polymeric material, fillers and at least one peroxide

for pre-cross-linkage and possibly process-promoting additives are compounded in a suitable apparatus such as, for example, an extruder, to produce a ground or granulate stock. For extruder compounding, a unidirectionally rotating ZE 40x39.5 D twin-screw extruder may be used, for example. The feed zone is heated to approximately 140° – 175°C, the further zones up to the nozzle to 195°C. The screw speed typically ranges from 60 to 80 rpm. The exiting slab is cooled in a water bath and granulated in the slab granulator. The granulate thus obtained, can be further ground to achieve certain structures prior to wetting with peroxide.

Subsequently, in step (b), the ground or granulate stock thus obtained (hereinafter also referred to as "particles") is wetted with a solution containing at least one organic peroxide that is free from aromatic hydrocarbons and, optionally, co-cross-linking agents and possibly process oil. This permits the migration of the peroxide and the co-cross-linking agent into the particles of the ground or granulate stock. The granulate mixture, the particles of which may differ in their degree of pre-cross-linking, is heated in a granulate drier to a temperature of about 50°C. The hot granulate is then introduced into a slow-running horizontal mixer and wetted with a liquid mixture of co-cross-linking agents and possibly process oil and mixed for about 30 minutes. This is followed by wetting with peroxide and possibly process oil and further mixing for about 10 minutes. After a total mixing time of about 40 minutes, the liquid mixture has diffused into the granulate particles. Prior to further processing, the granulate is then intermediately stored for at least 48 h, preferably in a heat insulated container for slower cooling.

In step (c) the particles are heated to about 50°C and then precompacted and shaped, for example in the nip of a two-roll mill. The rolls typically have a surface temperature of 130° – 170°C. The roll surface can be smooth or corrugated/crisscrossed. For the corrugated roll, the lower surface temperature

applies. The structure of the flat shape produced in the roll nip is a function of the diameter and the surface characteristics of the rolls. With smooth rolls, the structure is a function of the degree of pre-cross-linking. The mass in the bead, however, should not be hotter than the scorch temperature of the peroxide used in step (b). In this step, a coherent sheet without holes and with close weight tolerances per unit area across its width is usually produced. The surface of the rolled sheet, however, does not usually need to be smooth. A rough surface actually enhances breathing in the following process step.

In the next step (d) the material thus heated is smoothed and cross-linked in an apparatus, such as a twin press, multi-platen press, twin Auma or steel band Auma machine, at a suitable pressing power of, for example, 1.2 – 5 bar/cm<sup>2</sup> and at a temperature of, for example, 180° – 200°C, at which the half-life of the peroxide is reduced, such that simultaneous cross-linkage of the material initiated by the peroxide occurs. Due to the high heat capacity of the filled polymeric binder masses, the corresponding strips are usually preheated to a temperature of about 160°C prior to introducing them into the aforementioned apparatuses. The speed of the above Auma machines or presses is a function of the half-life of the employed peroxide at the correspondingly selected temperature within the strip cross-section as it passes through the machine.

In another embodiment, the addition of co-cross-linking agent(s) can occur already in step (a) without any further addition of co-cross-linking agent being required in step (b) as described above, which makes it possible to shorten the mixing time.

In a further embodiment, an excess of co-cross-linking agent, particularly trimethylolpropane trimethacrylate (TRIM) may be used. The molar ratio of peroxide to co-cross-linking agent is at least 1:4. The non-reacting TRIM excess acts as a processing aid and reduces the viscosity of the polymer melt prior to



the addition of peroxide in the extruder. In the subsequent processing step in the course of the production of the floor covering according to the invention, i.e. the wetting of the additionally ground extruder granulate with liquid peroxide and the subsequent cross-linking of the flat product, the TRIM contained in the particles reacts with the diffused peroxide. It is therefore unnecessary to rewet the ground stock with co-cross-linking agents. During pre-cross-linking in the compounding extruder, the following raw material addition sequence has proven to be suitable. Through the first metering orifice of the extruder, a master batch of additives, such as slip agents, antioxidants and static eliminators are added in addition to the polymer mixture. Here, too, a co-cross-linking master batch may be added, such as, for example, Perkalink 301-50 (a 50% preparation of triallyl isocyanurate). After the melting section in the extruder, the liquid co-cross-linking agent, such as, for example, TRIM, and possibly mineral oil, are added via an injection nozzle. To this polymer melt the viscosity of which is reduced due to the added liquids, the filler is added, for example via a lateral feed unit. Prior to feeding the filler into the polymer melt, it is preferably mixed with the pre-cross-linking peroxide in the form of a powdered master batch. This ensures uniform distribution of the reactive components. Between the lateral feed unit and the vacuum degasification unit on the extruder, a sufficiently long section for mixing and reaction can be disposed to promote uniform distribution through a specially adapted temperature profile and a specific design of the screw profile.

In another embodiment of the process according to the invention, instead of the shaping in the roll nip executed in step (c), the wetted particles can be distributed onto a leader and covered with an embossed anti-adhesive paper to produce a non-directional design of the floor covering. The granulate feed stock is compacted in the press while cross-linking and is pressed for a corresponding dwell time. Subsequently, the bottom leader and the top release paper can be pulled off.

In one embodiment of the process according to the invention, partially cross-linked particles based on the above-defined polymeric material comprising polyolefin and graft co-polymer are added to the uncross-linked mass to obtain a relief structure of the flat product after pressing in step (d). The partially cross-linked particles can be cross-linked to a varying degree. Partial cross-linking of the particles can occur during extruder compounding prior to granulation in the case of granulate. The partially cross-linked particles are only reversibly deformed during pressing, and after pressure release, due to the restoring forces, a high/low structure is obtained. The degree of cross-linkage of the partially cross-linked particles may be adjusted via the peroxide amount and the possibly used co-cross-linking agents.

In a further embodiment of the process according to the invention, in step (a), a cross-linkable mass based on the above-defined polymer materials is compounded with at least one cross-linking agent and possibly one of the above-defined additives. By controlling the dwell time in the extruder, and through a corresponding screw geometry, and overall length of the extruder it is possible to obtain a partially cross-linked granulate. This embodiment permits the production of patterns analogous to PVC technology. This means, for example, that a directional structure can be obtained. In this embodiment it is possible, in particular, to combine the mechanical properties of elastomer coverings with the visual/structural characteristics of PVC coverings.

By using an uncross-linked or partially cross-linked mass, i.e. a cross-linkable mass without peroxide or with a very small amount of peroxide, it is possible to control the course of the process via the migration of the peroxide used in the solution to sheathe the particles of ground or granulate stock. Furthermore, the multi-stage production process allows the use of equipment or apparatuses that are typically used in the soft PVC industry.

In another embodiment of the process according to the invention, the mass can be compounded in step (a) with an added chemical expanding agent, such as, for example, sulfohydrazides or azodicarbonamides or a combination therefore, e.g., Luvopor 1417 (Lehmann & Voss & Co.) or Tracel DB 145 (Tramaco GmbH). After cross-linking under pressure in step (d), foaming of the material is achieved by pressure release at a further increased temperature. This embodiment is particularly suitable for floor coverings with expanded backing.

To produce a foam granulate for coverings with integral structure, a mixture of the aforementioned polymers, additives, e.g., slip agents, antioxidants and static eliminators, fillers, peroxide, co-cross-linking agents, e.g., methacrylate or TAIC, and a chemical expanding agent, e.g., azodicarbonamide, are compounded in an extruder. By a corresponding extruder design and adapted operating conditions, the mixture is partially cross-linked in the extruder and expanded and then delivered through the extruder nozzle in the form of a foam. As with compact material, the slab is cooled in a water bath and granulated. The granulate thus obtained is further ground and dried and subsequently wetted with a mixture of liquid peroxide, co-cross-linking agents and mineral oil. The ground stock is distributed onto release paper, covered with a release paper and fed into a heated press or the like. The temperature and pressure are adjusted such that the particle bed becomes plastic along the heating surfaces and melts to form a closed surface. At the same time, the temperature initiates the decomposition of the peroxide whereby the outer layers simultaneously cross-link. The low pressing power and the onset of the cross-linking reaction prevent a compression of the foamed material in the core of the plate thus obtained. This is further supported by a correspondingly high pre-cross-linking of the foamed material. This makes it possible to provide an elastomer covering with an abrasion-resistant wear layer and, at the same time, reduced density and improved impact sound characteristics.

In the aforementioned apparatus, embossing may be carried out at the same time, preferably by using a corresponding release paper. The thermoplasticity of the mass that still exists prior to the actual cross-linkage is sufficient to smooth the rolled sheet or to form the embossing before the onset of the cross-linking reaction.

In a finishing step, depending on the quality of the rolled sheet obtained in step (c), the back of the covering may have to be ground for sizing. Furthermore, the structure or pattern of the cross-linked material may be revealed after exposing the surface by grinding and or splitting. To improve bondability, a corona treatment with primer application may be carried out.

Special, heterogeneous floor covering structures may also be provided based on the present invention. The lay characteristics can be positively influenced by a correspondingly adjusted degree of cross-linking of the individual layers. To secure this effect, a suitable measurement procedure was developed in the context of this invention. Samples of the corresponding structure and thickness measuring 250 mm x 250 mm are produced. Parallel to the sample edges, sensors for an incremental length-measuring system are pasted to the surface at a 90° angle. The sample is conditioned in a standard 23/50 environment on a glass plate powdered with talcum. Subsequently, the samples are exposed to changing temperatures (10° to 60°C) and humidity conditions (35% to 90% relative humidity) in a climactic chamber and the expansion behavior is recorded. This measuring method makes it possible to predict the lay behavior of a floor covering thus produced already in the development stage and to optimize the covering formula and the correspondingly adjusted process.

The following multi-layer structures were developed and tested by means of the aforementioned measurement procedure: a mixture of multicolored particles of different sizes was distributed over a homogenous, calandered substrate and

compacted. If desired, a transparent layer may be applied over it in the form of a distributed powder or by foil lamination. Alternatively, a conventional multilayer structure of different foils that are joined by applying pressure and heat may also be used. The multilayer structures, the cross-linking degree of which can be optimized by the described measurement procedure, further permit the production of dimensionally stable tiles based on the polymers used to make the floor covering according to the invention.

Even when producing the floor covering according to the invention in the form of a homogeneous covering by distributing granulate or ground stock over a strip with release properties, structure variants can be produced through the distribution of the corresponding particle fractions, i.e. by distributing first the basic color(s) and subsequently the particles in contrasting colors. This can be achieved in that the basic color is distributed over a substrate via a distributing unit with a brush roller uniformly arranged across the width. This applies the basic color in a weight distribution that is uniform over the width of the strip. The contrasting particles are then also distributed, but the distributing unit is preferably designed in such a way that different particle amounts are applied across the width of the strip. Subsequently, the particle bed is precompacted and fed into a heated press or the like. Alternatively, the two distributing units for the particle bed can be formed in such a way that a lesser amount of the basic color(s) is applied in the areas in which the contrasting particles are going to be distributed. When the contrasting particles are subsequently distributed, a particle bed that is uniform across the width is achieved. With this second variant, in particular, it is possible to achieve a non-warping structure and uniform thickness across the width of the strip even without precompaction. Other interesting structures can furthermore be achieved during installation by stamping two or four tiles of equal size across the width of the material.

The present invention will now be explained in greater detail by means of the following example.

### Example

A homogeneous mixture is produced and granulated from the following ingredients:

DOW DSH 1505	1875.0 g
DOW EG 8200	750.0 g
DOW XU 60769.07	375.0 g
Sillitin Z 89	1500.0 g
Omyacarb 6 BG	1125.0 g
Kronos 2200	375.0 g
Glycerol monostearate	48.0 g
Hostastat FA 14, 50%	12.0 g
Wax OP	36.0 g
Perkadox 14-40 BPD	10.2 g

The above formula was compounded in a type ZE 40 of the Berstoff company unidirectionally rotating twin-screw extruder with simultaneous pre-cross-linkage through the added peroxide. The cylinder temperature of the extruder in the feed zone was 145°C and in zones 3 – 9 195°C. The speed was 80 rpm.

The granulate thus obtained, after drying and preheating to 50°C, was wetted with a mixture of TAIC (triallyl isocyanurate) and TRIM (trimethylolpropane trimethacrylate) and mixed for about 20 minutes. Subsequently, a mixture of

Trigonox 101 and Dealen CP 31 N was added and mixed for another 10 minutes. The quantity ratios in relation to 500 g granulate were as follows:

TAIC	1.0 g
TRIM	3.0 g
Trigonox 101	4.0 g
Dealen CP 31 N	1.0 g

After a 48 h interim storage period, the wetted granulate was pressed into a plate in a static press at 140°C, and this plate was then also cross-linked in a press at 185°C for 10 minutes. Of this 140°C plate, a sample was measured on the Göttfert "Elastograph Vario" at 185°C. The adjusted measuring time was 12 minutes; the deformation angle was 0.4°. The T90 time for this mixture was 2.9 min.,  $T_{v_{max}}$  at 0.7 min.

In the test specimen of the elastograph, the indentation characteristic was measured in accordance with EN 433. The initial thickness was 6.35 mm, the indentation after 150 minutes was 0.27 mm, and the remaining indentation after release for 150 minutes was 0.01 mm. This results in an index of 4.3 and a recovery of 95.1%.

From the cross-linked plate, S2 rods were stamped. The Shore A hardness was 95, the Shore D hardness 46. The 2.23 mm thick S2 rod exhibited a load at break of 12.7 N/mm<sup>2</sup> and an elongation of 430%.

## Claims

1. Floor covering comprising as polymer binder at least one elastomer based on at least one polyolefin with a density  $< 0.910 \text{ g/cm}^3$ , and at least one grafted copolymer.
2. Floor covering as claimed in Claim 1, wherein the polyolefin has a density of  $0.85 - 0.892 \text{ g/cm}^3$ .
3. Floor covering as claimed in Claim 1 or 2, wherein the polyolefin is selected from among the class of VLD PE polymers.
4. Floor covering as claimed in any one of Claims 1 to 3, wherein the polyolefin is a mixture of at least two ethylene copolymers, wherein the ethylene copolymer mixture comprises a copolymer (a) as the main polymer with a density of  $0.89 - 0.91 \text{ g/cm}^3$  and a copolymer (b) to control rheology and elasticity with a density of  $0.86 - 0.88 \text{ g/cm}^3$  and an  $\text{MFI} > 3$ .
5. Floor covering as claimed in Claim 4, wherein the copolymers (a) and (b) are present at a weight ratio of 4:1 to 3:2.
6. Floor covering as claimed in Claims 4 and 5, wherein the copolymers (a) and (b) are copolymers of ethylene and octene.
7. Floor covering as claimed in any one of Claims 1 to 6, wherein the grafted copolymer is a grafted copolymer based on a HD polyethylene.



8. Floor covering as claimed in Claim 7, wherein the grafted copolymer is a maleic acid anhydride grafted HD polyethylene.
9. Floor covering as claimed in Claim 8, wherein the grafting degree is 1% to 5%.
10. Floor covering as claimed in any one of Claims 1 to 9, wherein the proportion of grafted copolymer in relation to the total weight of the polymeric binder is 5% to 25% by weight.
11. Floor covering as claimed in any one of Claims 1 to 10, wherein the elastomer is cross-linked with at least one cross-linking agent based on organic peroxides and possibly one or more co-cross-linking agents.
12. Floor covering as claimed in Claim 11, wherein isocyanuric acid derivatives and/or acrylate or methacrylate derivatives derived from polyols are used as co-cross-linking agents.
13. Floor covering as claimed in any one of Claims 1 to 12, which further contains fillers and/or pigments as well as possibly processing aids, antioxidants, static eliminators, UV stabilizers and slip agents.
14. Floor covering as claimed in Claim 13, wherein essentially a mixture of platelet-shaped and crystalline mineral intergrowths is used as filler.
15. Floor covering as claimed in any one of Claims 1 to 14 having a variable color pattern and a homogeneous design.
16. Process for producing a floor covering as claimed in any one of Claims 1 to 15, comprising the provision of a substrate in the form of a strip and the

application of the elastomers defined in Claims 1 to 14 to one side of the substrate.

17. Process for producing a floor covering as claimed in any one of Claims 1 to 15 comprising the following steps:
  - Wetting of particles with a solution containing at least one organic peroxide free from aromatic hydrocarbons and possibly one or several co-cross-linking agents and possibly process oil, wherein the particles contain the above-defined polymers, which form the polymeric binder of the floor covering according to the invention, either cross-linked or partially cross-linked in the form of a ground or granulate stock,
  - Heating of the particles to a temperature at which the peroxide has sufficiently long stability, wherein the particles are subsequently precompacted and shaped into a flat product, and
  - Pressing of the flat product thus obtained in a suitable apparatus at a temperature at which the half-life of the peroxide is reduced such that cross-linking initiated by the peroxide simultaneously occurs to obtain a flat end product.
18. Process as claimed in Claim 17, wherein the wetting of the particles is carried out such that, in a first step, the particles are wetted and mixed with one or several co-cross-linking agents and possibly process oil and subsequently, in a second step, are wetted and mixed with at least one organic peroxide free from aromatic hydrocarbons and possibly process oil.

## **DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION**

As the below named inventors, we hereby declare that:

Our residence, post office address and citizenship are as stated below next to our names;

We believe we are the original, first and joint inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled:

### **LOW-EMISSION FLOOR COVERING**

the specification of which was filed on 11 May 1999 as Application Serial No. PCT/EP99/03229.

We hereby state that we have reviewed and understand the contents of the above-identified specification, including the claims.

We acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

We hereby claim any foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) and/or any international priority benefits under Title 35, United States Code, §365 based on the following foreign and/or international application(s) listed below, and also identify below any foreign and/or international application(s) for patent or inventor's certificate having a filing date before that of the application(s) on which priority is claimed:

Prior Foreign Application(s): German Application 19821193.7, Filed: 12 May 1998

We hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, we acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing of the prior application and the national or PCT international filing date of this application:

Prior Application(s): None.

We hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

We hereby appoint: Louis T. Isaf, Registration No. 29,078; James F. Vaughan, Registration No. 31,889; Steven D. Kerr, Registration No. 32,472; David Scott Sudderth, Registration No. 34,026; John J. Timar, Registration No. 32,497; Michael A. Cicero, Registration No. 34,562; Jeffery B. Arnold, Registration No. 39,540; Judy Jarecki-Black, Registration No. 44,170; Lisa J. Moyles, Registration No. 40,737; Steven L. Schmid, Registration No. 39,358; and David Hayzer, Registration No. 44,170, having as their mailing address Womble Carlyle Sandridge & Rice, PLLC, P.O. Box 725388, Atlanta, Georgia 31139-9388, our attorneys with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to receive the patent, and to transact all business in the Patent Office connected therewith, all correspondence to be directed to the said James F. Vaughan, Womble Carlyle Sandridge & Rice, PLLC, P.O. Box 725388, Atlanta, Georgia 31139-9388.

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